U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-269 223

Evaluation of Continuous Monitoring Sites in EPA Region VI

Radian Corp, Austin, Tex

Prepared for

Environmental Protection Agency, Dallas, Tex Surveillance and Analysis Div

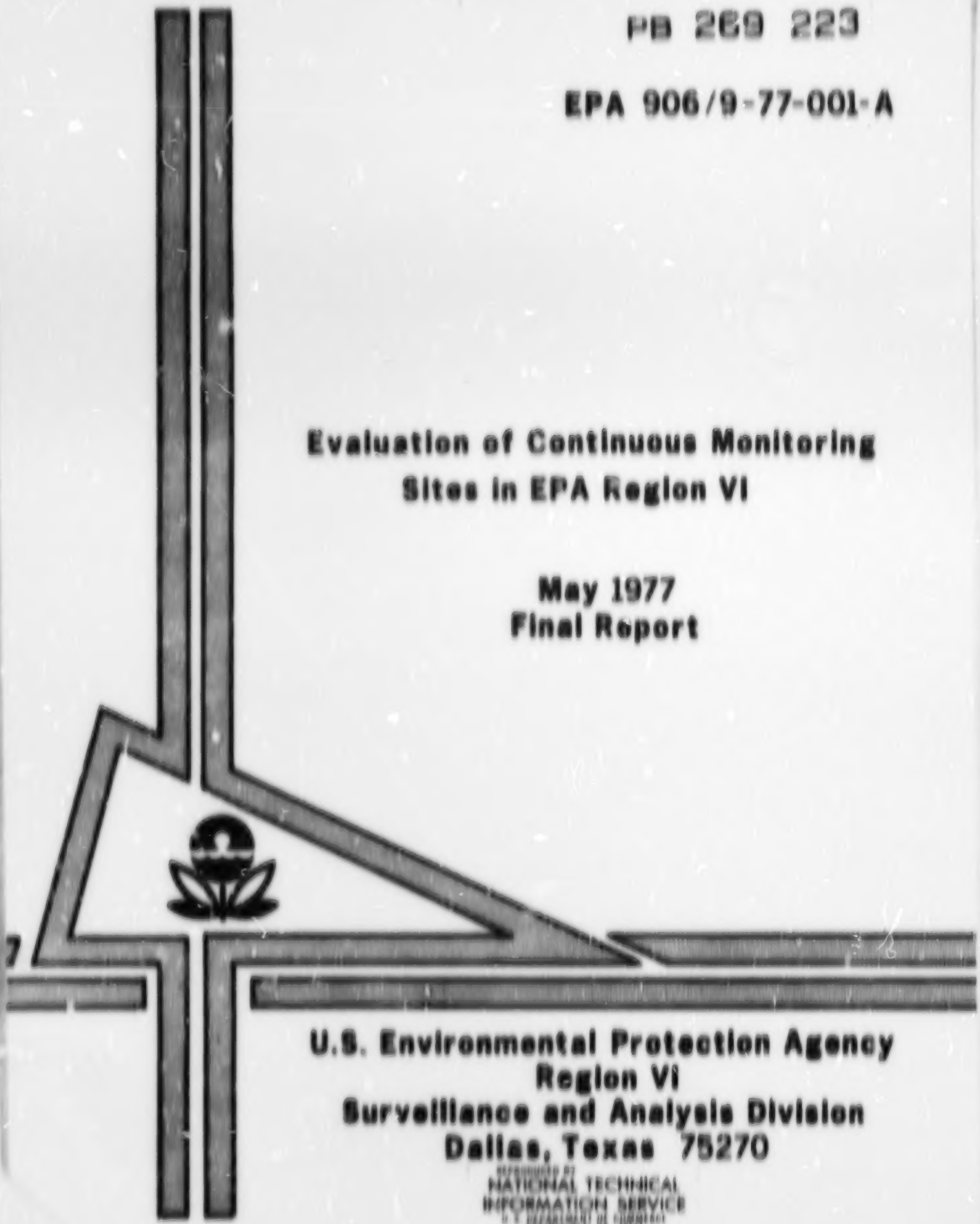
May 77

PB 269 223

EPA 906/9-77-001-A

Evaluation of Continuous Monitoring Sites in EPA Region VI

May 1977
Final Report



U.S. Environmental Protection Agency
Region VI
Surveillance and Analysis Division
Dallas, Texas 75270

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1 REPORT NO. EPA 906/9-77-001a	2	3 RECIPIENT'S ACCESSION NO
4 TITLE AND SUBTITLE Evaluation of Continuous Monitoring Sites in EPA Region VI		5 REPORT DATE May, 1977
7 AUTHOR(S) Radian Corporation		8 PERFORMING ORGANIZATION REPORT NO 100-044-16
9 PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation P.O. Box 9948 Austin, Texas 78766		10 PROGRAM ELEMENT NO
		11 CONTRACT/GRANT NO 68-02-1383, Task 16
12 SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Region VI 1201 Elm Street Dallas, Texas 75270		13 TYPE OF REPORT AND PERIOD COVERED Final
		14 SPONSORING AGENCY CODE

15 SUPPLEMENTARY NOTES

16 ABSTRACT

This report describes the methods and results of a quality assurance study of selected municipal and state air monitoring programs being conducted in EPA Region VI. The continuous analyzers that were evaluated were analyzers for ozone and carbon monoxide. The study involved a visit to each monitoring station to perform a systems analysis of the station, to evaluate the site, and to perform an audit of the continuous monitors using control gases. Data processing checks were also performed at the agency offices.

17 KEY WORDS AND DOCUMENT ANALYSIS

a DESCRIPTORS	b IDENTIFIERS/OPEN ENDED TERMS	c COSATI Field/Group
Quality Assurance Ambient Air Quality Monitoring Ozone Carbon Monoxide		

18 DISTRIBUTION STATEMENT Release Unlimited	19 SECURITY CLASS (This Report) Unclassified 20 SECURITY CLASS (This page) Unclassified	21 NO OF PAGES 47 22 PRICE

EPA Form 2220-1 (9-73)

DCN #77-100-044-16-04

EPA # 906/9-77-001a

EVALUATION OF CONTINUOUS MONITORING SITES IN EPA REGION VI

Prepared by:

Radian Corporation
P.O. Box 9948
Austin, Texas 78766

Contract No. 68-02-1381, Task Order 16

FINAL REPORT

Prepared for:

Tim Matske
Environmental Protection Agency
Region VI
Surveillance and Analysis Division
Dallas, Texas 75270

May, 1977

This air pollution report is issued by Region VI Environmental Protection Agency, to assist state and local air pollution control agencies in carrying out their program activities. Copies of this report may be obtained, for a nominal cost, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22151.

This report was furnished to the Environmental Protection Agency by Radian Corporation, Austin, Texas in fulfillment of Contract No. 68-02-1383, Task Order 16. This report has been reviewed by Region VI, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Region VI Publication No. 906/9-77-001

TABLE OF CONTENTS

		PAGE
1.0	INTRODUCTION	1
2.0	PROCEDURES	4
2.1	Ozone Audits	4
2.1.1	Ozone Source Verification by NBKI Method	9
2.2	Carbon Monoxide Audits	14
2.3	Data Processing Audits	15
2.4	Defects	17
3.0	CALIBRATION COMPARISONS	19
4.0	AUDIT RESULTS	23
4.1	Ozone Results	23
4.2	Carbon Monoxide	23
4.3	Data Processing Errors	31
4.4	Site Evaluations	34
5.0	DISCUSSION	35
6.0	SUMMARY	42

LIST OF TABLES

TABLE		PAGE
4-1	EPA Region VI Ozone Audit Results	24
4-2	EPA Region VI Carbon Monoxide Results	28
4-3	Accuracies of Retained Variables in City of Houston Continuous Monitoring Program	34
5-1	Summary of Guidelines for Probe Placement ..	37

LIST OF FIGURES

FIGURE		PAGE
2-1	Reverse Gas Phase Titration	13
2-2	Calibration or Audit of CO Analyzer Using Pressurized Gas	16

1.0 INTRODUCTION

This report describes the methods and results of a quality assurance study of selected municipal and state air monitoring programs being conducted in EPA Region VI. This study was performed as a part of Task Order 16 of Basic Ordering Agreement 68-02-1383. The study included high volume total suspended particulate samplers and continuous monitors for ozone and carbon monoxide; however, this report presents only the results for the continuous monitors.

For each monitoring station in each agency, the study involved a visit to the station to perform a systems analysis of the station, to evaluate the site, and to perform an audit (using control gases of known composition) of the continuous monitors. The agency office was also visited to perform data check audits for air quality data which had previously been reduced and converted to SAROAD format.

The state agencies included in this program were the following:

- Arkansas Department of Pollution Control and Ecology
- Louisiana Air Control Commission
- New Mexico Environmental Improvement Agency
- Oklahoma State Department of Health
- Texas Air Control Board

Municipal or county continuous monitoring programs were included for the following groups:

- Albuquerque Department of Environmental Health
- Oklahoma City-County Health Department
- Tulsa City-County Health Department
- Houston City Health Department
- El Paso City-County Health Department
- Dallas City Department of Public Health

Prior to initiation of the field work, each of these agencies was visited by representatives of Radian Corporation and EPA Region VI to explain the goals of the program and the procedures to be used.

Section 2 of this report describes the methods and procedures used in the study. Section 3 describes the numerous side-by-side calibrations which Radian performed during the program with other air monitoring agencies to assure that the methods and calibration gases used in this study were accurate. The results of the audit checks, station examinations, site evaluations, and data processing checks are presented in Section 4. A discussion and summary is provided in Section 5. The results of this study have been presented in a confidential manner to maintain objectivity. The purpose is to identify potential problems and areas that need improvement. The intent was not to validate data for that would require a regularly scheduled series of audit checks.

In addition to this report, Radian also provided the Environmental Protection Agency with two copies of files for each site visited. These files contain photographs and descriptions of the individual sites for future reference.

It should be noted that defects (a difference between a check value and an indicated value) as defined for this program are the best estimates available at this time, and are to be considered only as guidelines. The defects as outlined by the Environmental Protection Agency are defined in Section 2.

3.0 PROCEDURES

Included in this section are descriptions of (1) ozone audit procedures, (2) carbon monoxide audit procedures, (3) definitions of defects, and (4) data processing audit procedures.

3.1 Ozone Audits

The basis for the audits of the continuous ozone analyzers was on-site bubbling using neutral buffered potassium iodide (NBKI) as set forth in the Federal Register. This technique, although under intense scrutiny, is still the reference method for calibrating ozone analyzers.

Reverse gas phase titrations (RGPT) were periodically performed to compare NBKI curves before and after audit trips. After a standard NBKI curve had been obtained, a single point output from the ozone source would first be tested by the NBKI method, then titrated with NO gas and the results compared. The EPA has found the difference between gas phase titration methods and the NBKI method to range from 1% to 12% (Federal Register, Vol. 41, No. 195, Wednesday, October 6, 1976). Radian found that its differences between the two techniques were usually between 7% to 12%. This range is probably due to the precision of the NBKI method. After some audit trips, the two methods were used to verify that the NBKI had not changed during the audit period. Verification of the NBKI solution stability was done if there were serious discrepancies between the audit and indicated values. There was one instance at the initial visit to site 30 in which gas phase titration was used to verify that the NBKI solution was unstable. The results that were being obtained at site 30 with this particular solution appeared to be low and were somewhat erratic from one run to another. The RGPT equipment was set up at the site, and results confirmed

that indeed the ABKI solution was bad. If the ABKI becomes unstable, the solution will not completely absorb the O_3 and will lead to errors. The trip was aborted until fresh, standardized solution could be obtained, and the previous results using this solution were negated. The site was audited on another visit. This was the only instance in which difficulties were experienced with the NBKI method. However, there was another instance at sites 7 and 9 in which both ABKI and RGFT were used in an audit for comparison purposes.

Detailed descriptions of these two techniques are given below.

3.1.1 Ozone Source Verification by NBKI Method

Equipment List

Item	Quantity	Description
1	3	30 ml midget impingers
2	4	Glass fitting clamps
3	3	Adaptors/glass fittings to teflon tubing
4	1	Regulated flow vacuum source 800-1000 cc
5	1	ABS-traceable bubble flowmeter and stopper for vacuum source flow verification with stop watch
6	1	Assortment of teflon tubing for connecting impinger train to O_3 generator and vacuum source
7	1	Variable output O_3 generator, i.e., Bendix Portable Calibrator
8	1	Bausch & Lamb Spectronic 20 Spectrophotometer
9	1	Fresh quantity of recently standardized ABKI absorbing reagent with curve
10	2	Rectangular cuvettes - same as used in standardization procedure

Item	Quantity	Description
11	1	Package lint-free glassware towels
12	1	Thermometer or thermocouple bridge temperature indicating system

The Bendix Model 8861D Field Calibration System is designed to produce its own zero air. Ambient air is drawn into the calibrator via the particulate filter and pump. From the pump the air passes through a condenser, which condenses the moisture in the air, allowing the moisture to be collected in the water dropout, and effectively drying the air. The dried air then passes by the ultraviolet clean-up lamp which ozonates any NO in the incoming air, converting it to NO_2. From the clean-up lamp, the air passes into a reaction vessel (surge tank) which tends to smooth the incoming flow. From the reaction vessel, the air passes through the soda lime scrubber which removes any NO_2 and ozone in the air, then through a filter, providing zero air. The zero air either may be used directly as a source of clean air or it can be exposed to a controlled amount of ultraviolet light to produce ozone for calibration samples.

The Spectronic 20 is a durable, reliable instrument that meets the requirements of the ARKI method. However, it is recommended that it be used only with rectangular cuvettes. The test tube cuvettes that normally come with the instrument are too variable and too dependent on placement in the holder. The rectangular cuvettes which require an adaptor for the Spectronic 20 eliminate these problems.

Preparation

While the ozone generator was allowed to stabilize at the desired setting, the Spectronic 20 was warming-up. The

Spectronic 20 was checked for zero stability and full-scale response.

All impingers were checked to be sure they were clean, dry, and free of lint on the inside surfaces. If the impingers or tubing had not been recently used, the train was assembled without adding reagent and the vacuum source drew the O_3 sample output through tubing and glassware for several minutes so that any contaminants that might absorb or react with the O_3 would do so prior to the verification run. The vacuum source was equipped with an internal charcoal scrubber after the impinger train to protect valve seals, regulator ports, and pump diaphragms in the vacuum source from O_3 during the above cleaning procedure.

Vacuum Source Flow Verification

The vacuum source flow was verified just prior to the actual run or runs by taking several volumetric flowrate readings with a 1.0 liter bubble flowmeter. The flowmeter was a Hasting flowmeter with certification traceable to the National Bureau of Standards. Extreme flow values were discarded unless a vacuum source regulation problem was suspected. An average of the readings was corrected for the volumetric flowrate at 29.0°C and 1.0 atmosphere.

The correction was performed by taking a gas temperature reading inside the 1.0 liter flowmeter with the source connected. An equivalent vapor pressure figure was obtained from the flowmeter manual to allow for volumetric correction due to water present in the reservoir of the flowmeter.

The uncorrected barometric pressure was obtained from a reliable source such as the local weather bureau. The following equation was then used to correct the flowrate:

$$F_c = F_m \left(\frac{P_a - P_v}{P_s} \right) \left(\frac{298}{273 + T_a} \right)$$

where:

F_c = corrected volumetric flowrate
F_m = measured flowrate at sampling conditions
P_a = ambient barometric pressure
P_v = vapor pressure of water at T_a
P_s = standard pressure of 760 mm Hg
T_a = temperature of gas (measured)

<u>NBKI Absorbing Run</u>

A clean 10.0 ml pipet was rinsed with a small quantity of NBKI, and 10.0 ml of the reagent was accurately pipetted into each of the three impingers. The train was assembled carefully so that all fittings were pneumatically sealed. The output valve on the vacuum source was turned off and the train was connected to the O_3 generator's vented output and to the vacuum source. Simultaneously the vacuum source output valve was opened while starting a 10-minute timer or stop watch. The impinger bubbling action was rechecked since the impinger train with the reagent installed represents a fixed restriction between ambient and the source inlet.

While the 10-minute run was taking place, the spectrophotometer was adjusted. A wavelength setting of 352 nm was established and the scale endpoints set with zero light passage and blank NBKI solution. The cuvette was cleaned and also rinsed carefully with the reagent prior to using. The solution was inspected to be free of lint particles and small bubbles before readings were taken.

After the 10-minute run was completed, the train was disassembled and each impinger carefully turned while holding at an angle so that all solution on the sides of the glass would be remixed with the total volume.

Starting with the third impinger or the one furthest from the O_3 source, the absorbance readings were taken. Slightly over 5 ml of the exposed solution was used to carefully rinse the cuvette two or three times (using 1.5 to 2.0 ml per rinse) being careful to rinse all inside surfaces each time. The remaining solution was added in total and the absorbance reading was taken.

The three impingers were marked so that each one was kept in its respective position in the train during additional runs.

After all absorbance values were determined, the concentration of the source gas was determined by the following calculations.

1. Obtain equivalent μgO_3 readings for each of the three absorbances values from the UBKI standardization curve.

2. Total the three μgO_3 readings.

3. Let V_r = (10 minutes) (F_c) (10^{-3}) where V_r is the volume of air at reference conditions, F_c is the corrected volumetric flowrate, and ten minutes is the sample duration.

4. The ppm O_3 = $\frac{\text{total } \mu gO_3}{V_r} \times 5.10\ (10^{-1})$

All calculations are taken from the Federal Register procedure.

Timing is of relative importance in all steps of the NBKI O_3 source verification technique. Exposed solutions were read as quickly as possible without sacrificing cuvette cleanliness. The spectrophotometer was set and calibrated with zero and blank readings just prior to each set of sample readings. Also, once reagent was pipetted into the impinger train, the run was started as quickly as possible.

Two runs were obtained for each ozone generator setting. If the reading varied by more than eight percent, additional runs would be made as required.

2.1.2 Ozone Source Verification by Reverse Gas Phase Titration (ROPT)

Equipment

Item	Quantity	Description
1	1	Cylinder NO in N_2 gas concentration traceable to NBS.
2	1	Bendix Portable Dynamic Calibration System.
3	1	NBS-traceable bubble flowmeter with stopwatch.
4	1	Chemiluminescent continuous ozone analyzer.
5	1	Stainless two-stage regulator for NO in N_2 source gas cylinder.
6	1	Set of appropriate tubing and fittings for interconnection of the above equipment.

The zero air source is the same as that previously described for the NBKI procedure.

Two cylinders of nitric oxide in nitrogen were used in the RCPT's. The first was a Standard Reference Material cylinder obtained from the National Bureau of Standards; the second was an Airco cylinder which had been referenced to the NBS cylinder by comparing its response on a Meloy SA520 that had been calibrated with the NBS cylinder.

Preparation

A flow diagram of the RCPT procedure is given in Figure 2-1.

The ozone generator portion of the calibration system was allowed to stabilize at the desired setting for the time period recommended by the manufacturer. The ozone analyzer was functional and fully stabilized prior to starting the operation.

The analyzer was connected to the calibration system output through a vented manifold after a zero air output baseline had been established by either actual instrument adjustment to zero output or notation of the response to zero air. The zero air was obtained by drying the air, oxidizing NO to NO_2, and removing NO_2 and O_3 by scrubbing.

The total air flow from the calibrator was on the order of 2.0 to 3.5 liters per minute and was verified by measurement with the bubble flowmeter. The dilution air pressure gauge readings were noted at this time and held as nearly constant as possible. Dilution air flow was held constant throughout the entire operation.

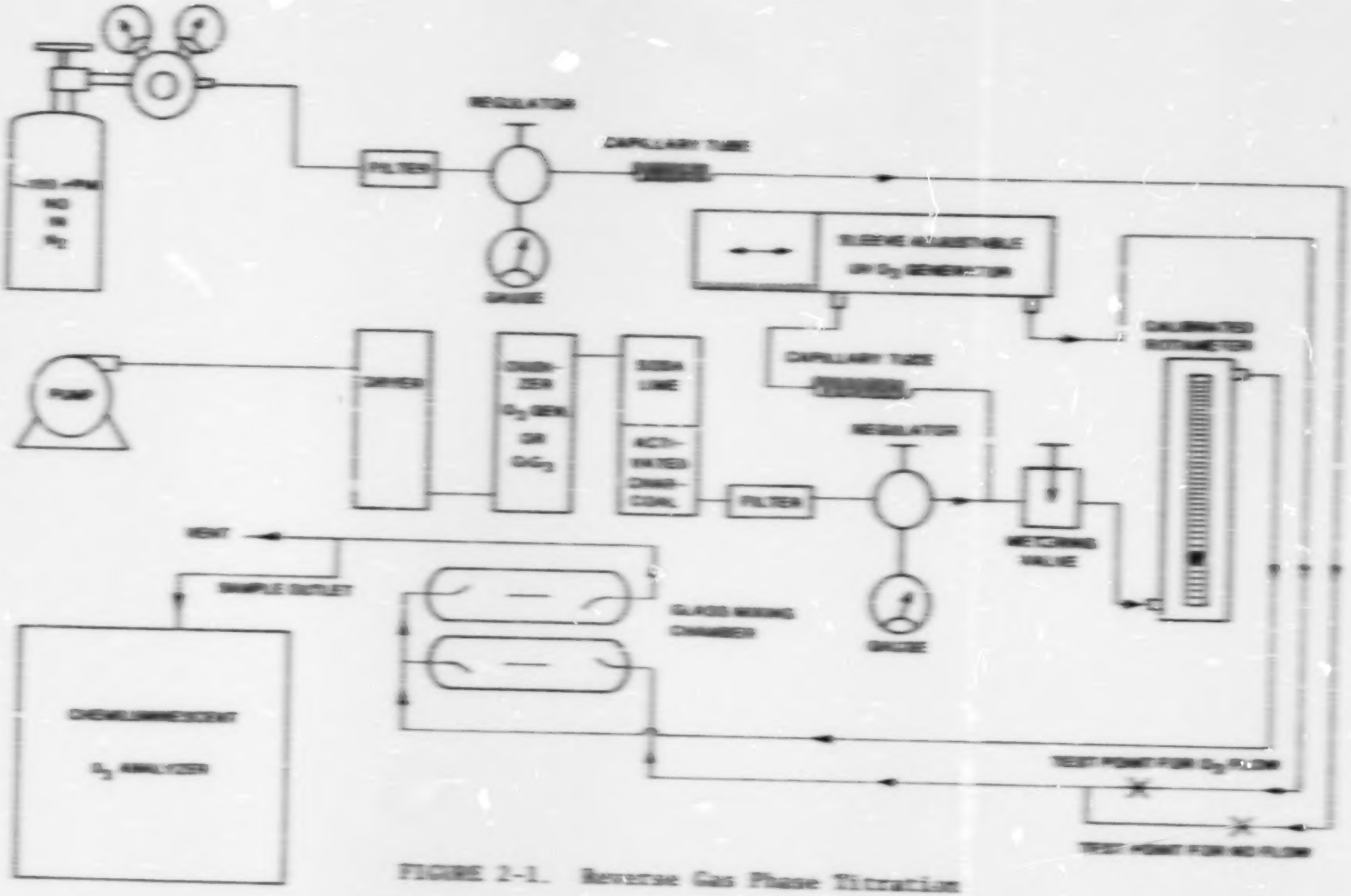


FIGURE 2-1. Reverse Gas Phase Titration

Gas Phase Titration Procedure

When the analyser response to the calibrator output was fully stabilised, this reading was noted as O_{3i} or initial ozone response.

The NO source line was purged completely and the required amount of NO source flow was then introduced into the O_3 stream ahead of the calibrator's first mixing chamber.

An approximate curve of NO source flow versus NO gauge reading is quite valuable at this point since it allows some operator control of the NO concentration being titrated into the O_3 gas stream. The NO concentration should be approximately 80 percent of the actual O_3 concentration, but since the actual O_3 concentration is not realized initially it must be assumed that the O_3 analyser is within 10 to 20 percent accuracy on its calibration settings so the O_{3i} may be used as an approximate indication of the actual O_3 output from the calibrator.

Since total dilution flow was known, the NO concentration was predicted by:

$$\text{NO ppm} = \frac{\text{NO source flow}}{\text{Total dilution flow}} \times \text{Source concentration}$$

In this equation the NO source flow was approximated by using a chosen gauge setting. After the titration had taken place for several minutes and the O_3 analysers response had stabilised completely at its new lower reading this was noted as O_{3f} or final ozone response.

Being careful not to change any pressure settings the NO source flow was immediately and accurately measured using the NBS-traceable bubble flowmeter.

If there was any doubt about the dilution air flow, it was also remeasured at this time.

The analyser was also checked to verify that its response returned to O_{3i} when the NO gas was removed from the O_3 stream.

The results of a single point titration may be calculated as follows:

$$O_{3a} = \frac{(NO)\ (O_{3i})}{O_{3i}-O_{3f}}; \text{ where } NO = \frac{NO_s}{TDA + NO_s}\ NO_g$$

where:

NO = resultant NO concentration added to O_3 stream.
O_{3a} = actual O_3 concentration of generator output
O_{3i} = initial analyzer response to generator
O_{3f} = final analyzer response during titration
NO_s = NO gas source flow; NO_g = NO cylinder concentration
TDA = total dilution airflow

2.3 Carbon Monoxide Audits

The continuous carbon monoxide analysers were audited by injecting samples of control gases into the analysers. Cylinders of audit gases contained ultra-pure air, high concentrations of CO in ultra-pure air, and low concentrations of CO in ultra-pure air. The audit gases were obtained from Scott-Marrin, Inc., and Scott Environmental Technology. The cylinders of ultra-pure air contained less than ten ppb carbon monoxide, total hydrocarbons, and oxides of nitrogen and less than one ppb sulfur dioxide. The control samples of carbon monoxide in air

were referenced to a cylinder of carbon monoxide in nitrogen obtained from the National Bureau of Standards. The NBS was-lined bottle was Standard Reference Material 1677a, cylinder No. FI00611 whose analysed concentration according to NBS was 9.82 ± 0.14 parts per million carbon monoxide by volume. The NBS cylinder was received May 5, 1976, at the start of the contract. The response of the cylinders of CO audit gas were compared to the response of the NBS cylinder on a Bendix 8200 Environmental Gas Chromatograph.

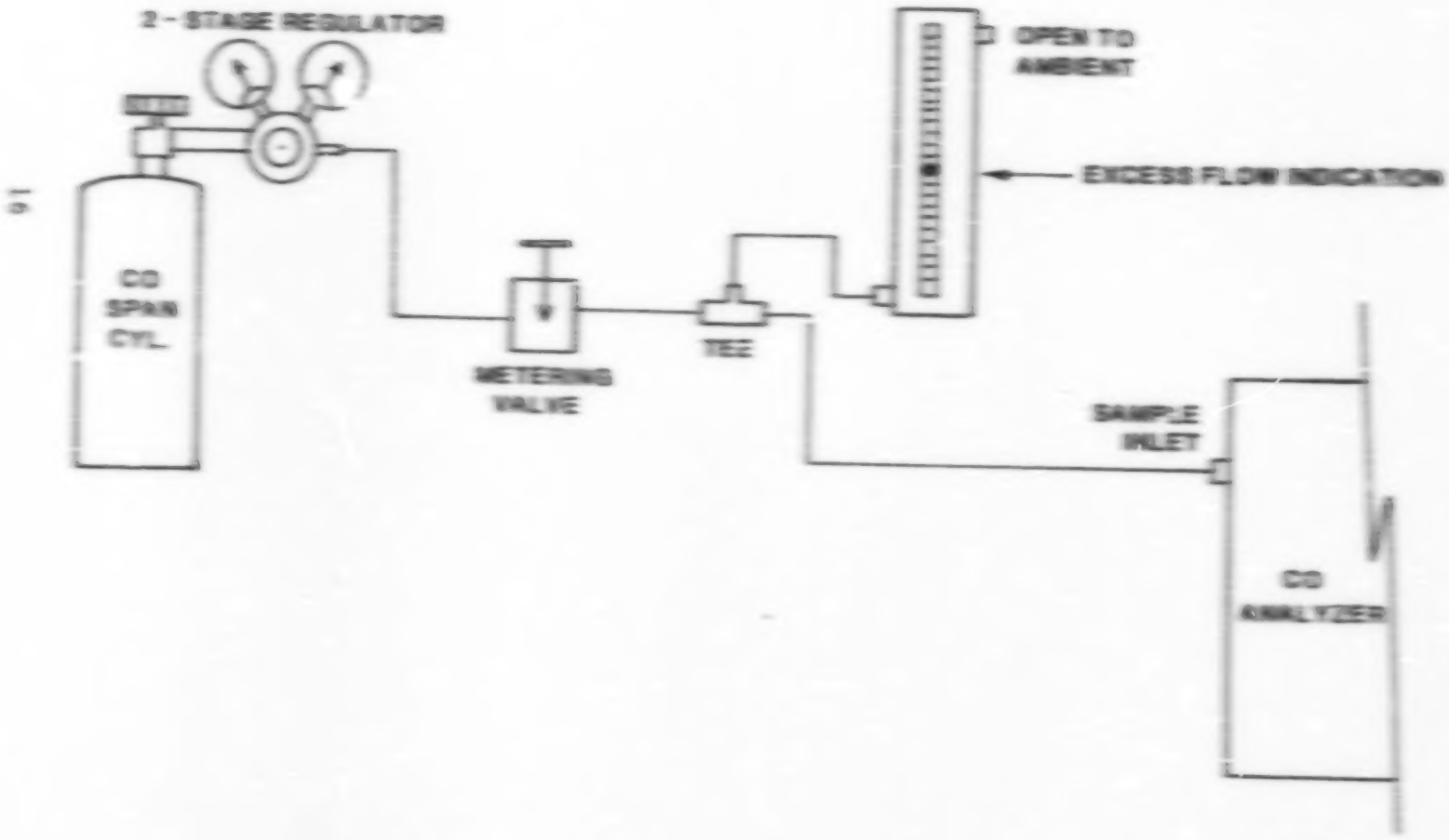
The audit gases were introduced as ambient samples at atmospheric pressure. The tubing and fitting used to connect the control sample to the analyzer were Teflon. To insure that the samples were introduced at atmospheric pressure, a tee was placed in the sample line with one part vented to the atmosphere through a rotameter. Sufficient flow through the rotameter maintained the sample at atmospheric pressure without having ambient air enter the system. A schematic of the injection process is shown in Figure 2-2.

2.3 Data Processing Audits

The data checks were to be conducted on the latest 100 days of data that had been reduced. These checks were performed in the agency offices. Seven days of data were selected for each analyzer, and two one-hour averages out of each 24 hour sampling period were checked. The checks were made starting with the strip chart record and continuing through the actual transcription of the concentration in ppm on the SAROAD form. This would then include reading, calculation, and transcribing or recording errors. The strip charts were measured using a K+E Compensating Polar Planimeter.

The data processing checks as outlined by the EPA were applicable only to those systems that recorded data on strip charts. Those agencies that used digital data acquisition systems are described separately in the results.

FIGURE 1-2. Diagram of
Calibration or Audit of CO Analyzer Using Pressurized Gas



3.4 Defects

Defects based on the difference between a check value and an indicated value were defined by the Environmental Protection Agency. These defects are based on the best estimates available at this time and are to be considered only as guidelines.

Only one type of comparison was made for ozone and that was a measurement of a control sample:

$$d_i = \frac{(\text{ppm } O_3)_m - (\text{ppm } O_3)_i}{(\text{ppm } O_3)_i} \times 100$$

where $(\text{ppm } O_3)_i$ was the true concentration as measured by the NBKI method and $(\text{ppm } O_3)_m$ was the concentration indicated by the analyser. A defect was defined as $d_i \geq 15\%$.

For the data processing checks, the difference between the check values, D_{ci}, and their corresponding original reduced values, D_{oi}, was determined as follows:

$$d_i = D_{ci} - D_{oi}$$

A defect was defined as $d_i \geq 0.010$ ppm.

Two types of measurements were made on the carbon monoxide analysers. The first was a comparison of a control sample to the analyser's response. For the measurement of the control sample:

$$d_i = C_b - C_a$$

where C_b was the unadjusted instrument value and C_a was the audit gas cylinder. The definition of a defect for this measurement is $d_1 \geq 2.2$ ppm.

The second CO measurement was a water vapor interference check:

$$d_1 = C_w - C_d$$

where C_w is the instrument response to saturated zero gas and C_d is the instrument response to dry zero gas. The definition of a defect is $d_1 \geq 1.7$ ppm.

The data processing check was:

$$d_1 = D_{ol} - D_{ol}$$

where D_{ol} was the check value and D_{ol} was the corresponding original reduced value. A defect here was defined as $d_1 \geq 1$ ppm.

3.0 CALIBRATION COMPARISONS

Radian has performed a number of side-by-side comparisons with a variety of agencies to establish the validity of calibration procedures. Because essentially the same methods are used by all agencies, the importance of the comparison studies is to verify the techniques of the parties involved. Radian has obtained excellent results in these comparisons particularly with respect to ozone measurements which are the most susceptible to variations in techniques. These results are also encouraging because of the number of different individuals that Radian has worked with in the past. During the visits when the program was being explained, Radian offered to conduct side-by-side audits or calibrations with any agency that so desired. The following paragraphs describe the results of recent side-by-side audits. A summary of the results is provided in Table 3-1.

Radian met with the Texas Air Control Board (TACB) for a comparison of ozone source verification techniques using neutral buffered potassium iodide (NBKI). This comparison was conducted May 10, 1976, in the TACB laboratories. This experiment yielded excellent agreement with all results closer than 5% difference which is good agreement. The system used by Radian consisted of a Radian constructed vacuum source, impingers, and a Bausch & Lomb Spectronic 20 spectrophotometer. A McMillan 1000 ozone generator was used as the ozone source. TACB employed a regulated vacuum system of their own construction, impingers, and a Bausch & Lomb Spectronic 88 spectrophotometer. Each part in the side-by-side employed its own NBKI solution which had been standardized in its own laboratories. Radian also compared its NBS-referenced cylinders of carbon monoxide against cylinders maintained by TACB.

Radian met with James Thompson of the Region VI EPA office on March 30, 1976, to compare techniques for ozone source verification. This experiment was conducted at the TACB monitoring station in Dallas. The results of the comparison were within 5% with Radian's results being consistently 2% to 5% lower than those obtained by Mr. Thompson. The equipment in this experiment was comparable to that used in the TACB study except that Mr. Thompson employed a Tylan variable flow controller.

Radian also met with Jim Thompson in Houston at the Region VI laboratories on May 20, 1976, for ozone source verification experiments by reverse gas phase titration. Both parties employed Bendix Dynamic Calibration systems of identical designs and NBS SRM NO cylinders of similar concentrations. Source verifications in these experiments agreed within 2%.

An additional NBKI source verification was performed by Radian against a calibration curve prepared previously by Mr. Thompson. As occurred in Dallas, Radian's values were 2% to 5% lower than Mr. Thompson's.

Radian conducted side-by-side audits at the St. Alma monitoring site with Jim Thompson and Alan Schmidt of EPA on August 19, 1976. The ozone comparison was within 5%. Radian employed NBKI source verification and Mr. Schmidt used a pre-verified calibrator curve. Radian also source-verified the output of the EPA calibrator and obtained good results for the values that were checked.

On October 20, 1976, and October 21, 1976, side-by-side calibrations were performed at the EPA Region VI laboratories in Houston. Comparisons were made between Radian, EPA Region VI, and a system from Research Triangle Institute (RTI)

Ozone comparisons by NBKI yielded reasonably good agreement. Reverse gas phase techniques yielded somewhat different results from RTI although Radian's results agreed with the Region VI system results probably because of equipment and procedure similarities.

4.0 AUDIT RESULTS

The quantitative results of the quality assurance audit checks for continuous ozone and carbon monoxide analyzers are given in the following paragraphs. These results are followed by a brief summary of the data processing checks and site evaluations. The results have been arranged in a random manner to maintain the confidentiality of the participating agencies. A discussion and summary of these findings are given in the following sections. Detailed results, including site photographs and site evaluations, are found in the individual file of site documentation presented to the Environmental Protection Agency.

4.1 Ozone Results

The instrument audit results for the continuous ozone analyzers are presented in Table 4-1. All ozone analyzers were chemiluminescent monitors. Of the 33 analyzers audited, six were found to have defects as defined by the EPA, and two were either malfunctioning or inoperative. One of the malfunctioning instruments was taking data at the time of the audit but was then taken off-line. This instrument was later re-audited and gave close agreement with the control samples. The second malfunctioning analyzer was inoperative at the time of the audit but was not taking data. Therefore, 18% of the analyzers were found to be in error and 6% were inoperative.

4.2 Carbon Monoxide

The instrument audits for the continuous carbon monoxide analyzers are presented in Table 4-2. Of the 29 analyzers that were audited, three instruments had defects as defined by the EPA, and six instruments were inoperative and in need of

TABLE 4-1

EPA REGION VI ICHMC AUDIT RESULTS

Station No.	Temperature Controlled	Manifold System	Meets EPA Sizing Criteria	Control Sample (ppb)	Instrument Response	Percent Difference	Defect	Comments
1	Yes	Conv.	Yes	181	169	-6.63	No	
				223	216	-4.04	No	
2	Yes	Conv.	Yes	181	189	+4.42	No	
				306	319	+4.25	No	
3	Yes	Tube	No	191	189	-1.05	No	
				247	237	-4.05	No	
4	No	Tube	Yes	155	217	+40	Yes	
				242	375	+55	Yes	
				183	143	+39	Yes	Re-audit
				198	260	+31	Yes	Re-audit
				312	385	+23	Yes	Re-audit
5	Yes	Tube	Yes	—	—	—	—	Malfunction
				179	185	+3.4	No	Re-audit
				234	245	+4.7	No	Re-audit
6	No	Tube	No	185	143	+36	Yes	
				258	358	+39	Yes	
				186	238	+25	Yes	Re-audit
				231	294	+27	Yes	Re-audit
7	No	Tube	Yes	109	111	+2.8	No	
				134	176	+1.5	No	
				195	174	-10.8	No	Re-audit
				226	174	-23	—	Re-audit NCPT

TABLE 4-1 (Cont'd)

EPA REGION VI AUDIT RESULTS

Station No.	Temperature Controlled	Manifold System	Meets EPA Siting Criteria	Control Sample (ppb)	Instrument Response	Percent Difference	Defect	Comments
8	No	Tube	Yes	159	115	-28	Yes	
				173	150	-13	—	Suspect Bubbling Error
				170	115	-35	Yes	RCPT
				223	152	-32	Yes	RCPT
9	Heat Only	Tube	Yes	135	120	-11	No	
				142	120	-15	No	
				228	223	-2	No	
10	Yes	Conv.	Yes	126	72	-43	Yes	
				130	72	-45	Yes	
				190	122	-36	Yes	
				205	122	-40	Yes	
11	No	Tube	Yes	159	105	-34	Yes	
				160	108	-32	Yes	
				300	237	-29	Yes	
12	Yes	Tube	Yes	102	115	+13	No	
				173	190	+9	No	
13	—	—	—	—	—	—	—	Malfunction
14	Yes	Conv.	Yes	128	160	+25	Yes	
				469	574	+22	Yes	
15	Yes	Conv.	Yes	197	197	0	No	
				438	378	-1.4	No	

TABLE 4-1 (Cont'd)

[illegible] AUDIT RESULTS

Station No.	Temperature Controlled	Manifold System	Meets EPA Sizing Criteria	Control Sample (ppb)	Instrument Response	Percent Difference	Defect	Comments
16	Yes	Conv.	Yes	403	416	+3.2	No	
17	Yes	Conv.	Yes	186	167	-10.2	No	
				290	313	7.9	No	
18	Yes	Conv.	Yes	186	190	+2.2	No	
				324	354	+9.3	No	
19	Yes	Conv.	Yes	178	164	-7.9	No	
				296	318	+7.6	No	
20	Yes	Conv.	Yes	196	226	+13.4	No	
				378	436	+14.8	No	
21	Yes	Conv.	Yes	178	176	+1.1	No	
				315	367	+18.3	No	
22	Yes	Conv.	Yes	152	178	-8.33	No	
				319	338	+6.1	No	
23	Yes	Conv.	Yes	196	175	-5.9	No	
				316	324	+2.5	No	
24	Yes	Conv.	Yes	176	168	-4.5	No	
				386	407	+5.4	No	
25	Yes	Conv.	Yes	180	174	-3.3	No	
				394	384	-2.5	No	
26	Yes	Conv.	Yes	186	153	-17.7	Yes	
				484	312	-22.8	Yes	

TABLE 4-1 (Cont'd)

EPA REGION VI AUDIT RESULTS

Station No.	Temperature Controlled	Manifold System	Meets EPA Siting Criteria	Control Sample (ppb)	Instrument Response	Percent Difference	Defect	Comments
27	Yes	Conv.	Yes	290	287	+8.4	No	
				351	375	+6.8	No	
28	Yes	Conv.	Yes	190	205	+7.9	No	
				305	313	+2.6	No	
29	Yes	Conv.	Yes	190	199	5.0	No	
				362	355	-1.9	No	
30	Yes	Conv.	Yes	187	230	+23.0	Yes	
				215	271	+26.0	Yes	
31	Yes	Conv.	Yes	185	196	+6.0	No	
				259	262	+1.2	No	
32	Yes	Conv.	Yes	164	175	+6.6	No	
				424	437	+3.1	No	
33	No	Tube	Yes	156	124	-25.5	Yes	
				200	154	-23.0	Yes	

Sites 3 and 6 did not meet siting criteria because the probes were mounted along and ran close to vertical walls. See discussion in the text.

TABLE 4-2

[illegible] SECTION VI CARBON MONOXIDE RESULTS

Station No.	Temperature Controlled	Manifold System	Meets EPA Sizing Criteria	Error at Time of Audit; Δ_1 C_a-C_b	Defect	Water Vapor Check Δ_2 C_a-C_d (ppm)	Defect	Comment
1	—	—	—	—	—	—	—	Deactivated
2	Yes	Conv.	Yes	—	—	—	—	Malfunction
3	Yes	Tube	No	—	—	—	—	Malfunction
4	Yes	Tube	No	0.2 ppm	No	0.9	No	
				1.9 ppm	No		No	
5	No	Tube	No	0.6 ppm	No	0.8	No	
				1.9	No			
6	Yes	Tube	No	—	—	—	—	Malfunction
7	No	Tube	No	1.2 ppm	No	1.1	No	
				3.9 ppm	Yes			
8	Yes	Tube	No	0.3 ppm	No	0.9	No	
				0.6 ppm	No			
9	No	Tube	No	0.3 ppm	No	0.8	No	
				0.6 ppm	No			
10	No	Tube	No	—	—	—	—	Malfunction
11	Yes	Conv.	No	0.7 ppm	No	0	No	
				3.2 ppm	Yes			
12	—	—	—	—	—	—	—	Malfunction
13	Yes	Conv.	Yes	0.7 ppm	No	1.0	No	
				0	No			
14	—	—	—	—	—	—	—	Malfunction
15	Yes	Conv.	Yes	1.3 ppm	No			
				0.3 ppm	No			

TABLE 4-2 (Continued)

EPA METHOD 11 CARBON MONOXIDE RESULTS

Station No.	Temperature Controlling	Manifold System	Meets EPA Siting Criteria	Error at Time of Audit; d_z<C_g-C_z	Defect	Water Vapor Check d_z<C_g-C_z (ppm)	Defect	Comment
16	Yes	Conv.	Yes	2.1 ppm	No	—	—	
				2.9 ppm	Yes			
17	Yes	Conv.	Yes	1.5 ppm	No	—	—	
18	Yes	Conv.	Yes	1.6 ppm	No	—	—	
				2.1 ppm	No			
19	Yes	Conv.	Yes	0.5 ppm	No	—	—	
				0.7 ppm	No			
20	Yes	Conv.	Yes	0.4 ppm	No	—	—	
				1.6 ppm	No			
21	Yes	Conv.	Yes	0.3 ppm	No	—	—	
				0.1 ppm	No			
22	Yes	Conv.	Yes	0.5 ppm	No	—	—	
				0.4 ppm	No			
23	Yes	Conv.	Yes	1.0 ppm	No	—	—	
				0.9 ppm	No			
24	Yes	Conv.	Yes	0.2 ppm	No	—	—	
				0.9 ppm	No			
25	Yes	Conv.	Yes	0.3 ppm	No	—	—	
				0.8 ppm	No			
26	Yes	Conv.	Yes	1.0 ppm	No	—	—	
				1.7 ppm	No			
27	Yes	Conv.	No	0.9 ppm	No	—	—	
				0.9 ppm	No			
28	Yes	Conv.	Yes	0.4 ppm	No	—	—	
				0.81 ppm	Yes			

TABLE 4-2 (Continued)

EPA AUDIT OF CARBON MONOXIDE RESULTS

Station No.	Temperature Controlled	Manifold System	Meets EPA Siting Criteria	Error at Time of Audit; $\Delta_1 = C_E - C_O$	Defect	Water Vapor Check $\Delta_2 = C_E - C_E$ (ppm)	Defect	Comment
29	No	Tube	Yes	4.1 ppm	No	0.7	No	See Note 1
				5.4 ppm	No			See Note 1

The sites that did not conform to EPA siting guidelines were out of compliance because the inlet probe was too high above ground level. See discussion in the text.

Note 1. Just prior to the audit at Site 29, the analyzer was inadvertently zeroed at the wrong point on the strip chart recorder. The result was that all readings were 5.0 ppm too low. Making this correction, the true results were 9.5 ppm and 10.25 ppm and the analyzer was, therefore, within the defect limits. After the audit, the analyzer was re-zeroed at the correct point and rechecked with the audit gases. All ambient data before and after the audit was correct.

repairs. Two of the analyzers that reported defects had defects only at the higher control sample concentrations. Therefore, 10% of the analyzers were in error and 21% were inoperative.

4.3 Data Processing Errors

Data processing checks were made to determine the accuracy of reducing data from the strip charts to SAROAD format. No gross errors were found in any of the systems. All defects that were discovered were due to operator error such as misreading the chart or incorrectly transcribing the data to SAROAD format. The main criticism of the strip chart reduction is the precision with which it is done. The usual case is to visually observe the data and make an estimate of the hourly average. Visual inspection techniques most often led to error when there were sudden changes in concentration or a series of spikes.

The most serious flaw found during the processing check was one of bookkeeping. At agencies using strip chart recorders it was often difficult and occassionally even impossible to match strip chart records with the corresponding SAROAD data. Strip charts were often not labeled or not recorded with enough detail to properly identify them or their data. Station identity, dates, times, and zero/span data were not well documented. The charts were often not separated by analyzer and/or maintained in chronological order in the filing system.

A summary of the problems encountered during the data processing audits are summarized as follows:

- Strip charts were often labeled with insufficient identification or descriptive detail.

- Strip charts were not filed in an organized manner after the data had been reduced.

- Strip chart data could not be found for some periods of time.

- In one instance, the data was reduced correctly, but assigned to the wrong hour on the SAROAD format.

- A new employee was responsible for one set of errors in the data reduction process.

- The visual averaging of values for hourly averages resulted in a number of errors. This was most common for CO when the hour contained a number of sharp peaks.

  Defects were more common for carbon monoxide than ozone because of the defect limits, strip chart precision, and the fact that CO levels change much more rapidly than ozone levels.

The data processing audit procedures outlined by the Environmental Protection Agency did not apply to the Texas Air Control Board and City of Houston systems since they do not employ strip chart recorders for data acquisition. These systems use digital data acquisition equipment with the final data reduction by computer. This eliminates many of the problems ordinarily associated with strip charts and increases the precision and accuracy.

The data processing centers of both Houston and TACB were visited by Radian personnel. The following paragraphs briefly describe the two data acquisition systems.

The City of Houston Health Department currently operates seven continuous monitoring stations. All monitored data are telemetered to the main office for processing. Each site is capable of analyzing sulfur dioxide, carbon monoxide, nonmethane hydrocarbons, photochemical oxidants, nitrogen dioxide, coefficient of haze, nitric oxide, total oxides of nitrogen, hydrogen sulfide, total sulfur, methane, total hydrocarbons, wind speed, wind direction, temperature, relative humidity, and rainfall on a continuous basis. Each of these channels is sampled once every five (5) minutes, converted from analog-to-digital signal, and transmitted to an IBM System 7 computer system via leased telephone lines. Each monitoring station is equipped with a data logger. Each sample is converted from the input voltage value to engineering units via calibration data stored on the System 7 disk. The calibration data must be manually updated by the site operators. The data is transmitted to the central facility as four digits plus sign. The maximum possible quantization error that can be experienced in this case is one part in 1000 or 0.01% of full scale. In general, the instrument accuracies are only ±2%, therefore, quantization or roundoff errors in the analog-to-digital conversion are much less than instrument inaccuracies. The input voltages are converted to engineering units utilizing the calibration data. Table 4-3 shows the retained accuracies of the conversion process. In summary, the possible data processing errors for the City of Houston's automatic data acquisition system are within the accuracies of the monitoring instruments.

TABLE 4-1

ACCURACIES OF RETAINED VARIABLES IN
CITY OF HOUSTON CONTINUOUS MONITORING PROGRAM

Parameter	Accuracy
Ozone	±1 ppb
Carbon Monoxide	±10 ppb

The Texas Air Control Board is currently operating 14 continuous air monitoring stations. Each of the stations automatically monitors and records each channel every five minutes. Each monitoring station is equipped with a data logger and a teletype. The teletype converts the signal from the data logger and reproduces five minute values on a hard copy printout and a paper tape. The five minute samples are punched into paper tape for further data analysis and reduction in the central office in Austin, Texas. The analog voltages are digitized to an accuracy of ±1 millivolt which indicates that data acquisition system is accurate to ±.1% of full scale. This accuracy compares favorably with most monitoring instruments whose accuracy are generally ±2% of full scale. The paper tapes are preprocessed at the TACB's computer, and a Univac 1106 is used for data storage and analysis. The data processing techniques of the TACB continuous monitoring systems are more accurate than analytical system accuracies. The paper tape that is processed in Austin is backed up by a hard copy printout.

4.4 Site Evaluations

Two ozone and ten carbon monoxide stations were classified as not meeting EPA criteria because of probe location. Other potential problems that were encountered were inadequate monitoring environments and questionable means of sample conveyance. The site conditions are discussed in more detail in the following section.

5.0 DISCUSSION

The overall goal of the monitoring programs should be the collection of data of documented precision, accuracy, completeness, and area representation so that the data can be used to confidently make air resource management decisions. The following items are essential to the collection of reliable air quality data:

- Stable, well-maintained instruments
- Reliable reference gases
- A regular quality assurance program including calibrations and frequent zero and span checks
- A sampling system composed of inert materials and of a design which will reliably provide sample of ambient air
- Cleanliness and proper operating procedures
- Detailed operating records
- Proper siting and design of the monitoring stations

The level and sophistication of the monitoring networks in EPA Region VI varies widely from one agency to another, and the capability to simultaneously meet the above criteria varies accordingly. The instrument audit checks were generally good, but there were limitations in several cases that bear further discussion. The purpose of this program, as stated

previously, was not to validate or invalidate data but to identify defects and potential problems. Detailed accounts of all audit results, site evaluations, and potential problems are given in the files for each site.

Two ozone stations (Sites 3 and 6) and ten carbon monoxide stations (Sites 3, 4, 5, 6, 7, 8, 9, 10, 11, and 27) were classified as not conforming to EPA siting and design criteria. These judgements were all based upon the probe location. The basis for these decisions was the EPA document "Guidance for Air Quality Monitoring Network Design and Instrument Siting," OAQPS No. 1.2-012, September, 1975. The criteria for monitoring different pollutants are summarized in Table II-5 of the above document. The guidelines for ozone and carbon monoxide probe inlets are shown in Table 5-1.

Because of the intrinsic variables noted in the spatial and temporal distribution of secondary pollutants such as ozone, specific recommendations with respect to probe height are deliberately general. The two ozone sites (Sites 3 and 6) that were classified as not meeting EPA criteria were disqualified because the inlet probes were located along large vertical walls. These sites are discouraged because wind obstructions completely block airflow from one direction, because of the variability in unknown vertical currents along the surface, and because of surface interactions that may scavenge ozone. Site 3 was also located more than 15 meters above the ground.

Specific probe heights or ranges of probe heights are recommended only for the primary pollutants such as carbon monoxide. Carbon monoxide monitoring sites may be classifed as (1) street canyon, (2) neighborhood, or (3) background. Inlet heights of 2.5 to 3.5 meters above the ground are recommended for street canyon and neighborhood monitors while a height of

TABLE 5-1

SUMMARY OF GUIDELINES FOR PROBE PLACEMENT

Pollutant	Site Type	Height Above Ground (Meters)	Vertical Clearance[a] (Meters)	Horizontal[b] Clearance (Meters)
Ozone	Peak	3 to 15	1 to 2	>2
	Neighborhood	3 to 15	1 to 2	>2
	Background	3 to 15	1 to 2	>2
Carbon Monoxide	Street-Canyon	3 ± 1/2	1	>2
	Neighborhood	3 ± 1/2	1	>2
	Corridor	3 ± 1/2	1	>2
	Background	3 to 10	1	>2

[a] Vertical clearance above rooftop or other supporting structure.

[b] Horizontal clearance from side of supporting structure or other restrictions to airflow.

three to ten meters is recommended for background monitors. The steep vertical gradients of CO concentration make it necessary to standardize the height of the probe above the ground so that these data collected will be comparable to data collected at other stations.

While neighborhood CO inlet heights are specified to be between 2.5 and 3.5 meters, more flexibility was allowed since the expected gradient with height is less than in the street-canyon situation. However, all agencies in Region VI should re-examine the location of their CO inlet probes with respect to EPA guidelines.

Background sites are classified as sites that should be 3 to 6 km from any interurban highway carrying 3,000 cars/peak hour and 400 meters from any road carrying over 100 cars/day. The background site should also be 35 km downwind in the least frequent direction from the urban area. Most stations in Region VI will, therefore, fall into the category of neighborhood or street-canyon sites. As such, they are subject to the more closely specified probe heights. Physical limitations will, in many instances, however, make meeting the 2.5 to 3.5 guidelines impractical.

Conditions exist at stations in Region VI which do not disqualify them but which make their operation at this time marginal. Because EPA siting guidelines are becoming more stringent, the agencies should consider upgrading their monitoring stations. The conditions that most often make the stations and their data marginal are primarily conditions that determine the adequacy of the monitoring environment. One of the most important factors in ambient air monitoring is to provide the instrument with a shelter that maintains a controlled

temperature and environment. The proper operating conditions, especially temperature, are necessary to minimize instrument drift and electronic malfunctions.

The Environmental Protection Agency has underlined the importance of temperature control in the certification of analyzers as equivalent methods. To be certified as an equivalent method, an approved analyzer must be operated between 20°C and 30°C. Cases were encountered in Region VI in which analyzers were subject to no temperature control or to inadequate temperature control. Some of the stations with no temperature control were in locations that can undergo wide temperature changes during a day and sometimes even within the span of a few hours. Such changes can lead to instrument instability and unreliable data. Ozone stations that had either no temperature control or inadequate temperature control were Sites 4, 6, 7, 8, 9, 11, 33 (Table 4-1). Carbon monoxide monitoring stations that had either no temperature control or inadequate temperature control were Sites 5, 7, 9, 10, and 29 (Table 4-2).

There were also cases where dusty, dirty conditions existed. Dusty equipment typically leads to electrical noise and instability, and dirty tubing can result in altered pollutant concentrations. On two occasions, analyzers were located in storerooms containing strong chemicals such as paints, solvents, or disinfectants.

The sample conveyance method at a number of stations should be improved. Many stations do not have a manifold, but use a long teflon tube and rely upon the analyzer's internal pump to pull the sample from the ambient air. The objection is that often the tubing is too long for this sort of arrangement. It was also noted at one series of stations that ground glass joints were used in the manifold system. These parts should be replaced by a manifold that joins the glassware with teflon bushings.

The instrument audits were generally good and are interesting when the results for the ozone and carbon monoxide analysers are compared. The results give clues as to the reliability of the instruments and to the importance of calibration procedures. Eighteen percent of the ozone analysers were found to be in error, and six percent were inoperative. Ten percent of the CO analysers were in error, and twenty-one percent were inoperative.

Calibrations and span checks for carbon monoxide analysers are much easier than for ozone analysers because of the availability of cylinders of carbon monoxide. No such source of reliable span gas is available for ozone; special equipment and techniques are necessary to generate control samples. The availability of control samples makes it easier to correct the CO analysers for drift and to identify when instruments are malfunctioning.

The defects in the instrument audits were most often due to drift or to calibrations. Upon reviewing the previous zero and span checks, the analyser at Site 4 was noted to have drifted almost 30% since its previous calibration. On another occasion, the CO analyzer at Site 29 was functioning correctly, but in performing a zero-span cycle just prior to the audit, the operator incorrectly zeroed the instrument on the strip chart. All data previous to this was good, and the instrument was correctly rezeroed during the audit.

This program demonstrates the need for a continuing quality assurance program for the agencies in Region VI. The monitoring network of one agency has an outstanding internal quality assurance program providing for frequent zero and span checks, multi-point calibrations, and audits. Other agencies need to develop quality assurance programs that include regularly

scheduled multi-point calibrations and audit checks to insure the reliability of their data and to provide a mechanism for the validation of data.

The data processing schemes of those agencies utilizing strip chart recorders should be improved. The strip charts should be better identified and contain more information. As much information as possible as to dates, times, calibrations, span checks, and unusual occurrences should be included on the strip charts. This data will aid those personnel reducing the data and lead to more reliable results. It should also be possible to improve the precision with which the strip chart data is reduced. Presently, an "eyeball" average is taken for each hour. This can lead to large error when there are sudden changes in concentration or a series of spikes. Also, it leads to stating concentrations in incremental units such as 5 ppb for ozone and 1 ppm for CO. This method of storing strip chart records should be improved at those agencies that employ these methods. The strip charts should be labelled with sufficient detail to identify location and times. They should then be stored in chronological order by monitoring site.

More detailed discussions and descriptions of the above points are included in the files for each site. Many of the problems with the individual monitoring stations arise due to site availability. The issues of network design and instrument siting involve difficult tradeoffs between air quality information needs and available resources, and between demands for data representativeness and instrument site availability.

6.0 SUMMARY

The following is a list summarizing the results of this program:

- 18% of the ozone analysers had defects as defined by the EPA.
- 6% of the ozone analysers were malfunctioning.
- 10% of the carbon monoxide analysers had defects as defined by the EPA.
- 21% of the carbon monoxide analysers were inoperative.
- Carbon monoxide monitoring sites do not meet the EPA guidelines of probe inlet heights of 2.5 to 3.5 meters above the ground.
- Ozone inlet probes were mounted, in some cases, along vertical walls.
- Temperature control is needed for some stations.
- Manifolds and sample conveyances should be improved.
- Better bookkeeping is required for maintaining strip chart records.